37

SINGLET→TRIPLET ABSORPTION IN META- AND PARACHLOROTOLUENE

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ABSTRACT. The absorption spectra of semi-transparent thick masses of *p*-chlorotoluene and *m*-chlorotoluene obtained by lowering the temperature of the liquids slowly upto about −130°C have been investigated. In the case of the first compound five broad bands at 26200, 26810, 27230, 27750 and 28260 cm^{-1} have been observed. Taking the first band as the (0, 0) band, the excited state vibration frequencies 610, 1030 and 1550 cm^{-1} have been derived. It has been pointed out that these frequencies correspond respectively to the frequencies 634, 1090 and 1596 cm^{-1} of the unsymmetrical modes of the molecule in the ground state and that in the fluorescence spectrum the 0, 0 band is absent.

In the case of metachlorotoluene only four weak bands at 24885, 25830, 26775 and 27720 cm^{-1} have been observed. The position of the first band is almost the same as that of the first broad band in the fluorescence spectrum of the molecule and if this band is taken as the 0, 0 band, a progression of the excited state frequency 945 cm^{-1} is given by the other bands. This corresponds to the frequency 996 cm^{-1} of the symmetric mode of the molecule in the ground state. It has been concluded that when the substitutions take place at positions which make the ring unsymmetrical the symmetric mode of the ring is coupled predominantly to the singlet-triplet transition in absorption and in the case of the para-substituted molecule vibration modes asymmetric to some two-fold axes of the ring are coupled to the transition.

INTRODUCTION

It was observed by Paul and Sirkar (1963) that the absroption spectrum of solid mass of *p*-bromotoluene of thickness about 7 mm. obtained by cooling the liquid very slowly to low temperatures shows weak absorption bands in the region 4045A—3603A. They concluded from the analysis of the bands that they are due to singlet→triplet transition. From a comparison of the positions of the bands with those of the fluorescence bands reported by previous workers they pointed out that the 0, 0 band does not appear in the fluorescence spectrum of this compound and that the vibration frequency 1516 cm^{-1} is coupled to the electronic transition in absorption. As chlorotoluenes in the solid state at low temperatures also exhibit strong luminescence which is excited by radiation of wavelengths shorter than 3750A but longer than 3000A (Roy, 1959), the luminescence is produced by excitation from the singlet state to the triplet state followed by transition to the singlet state again. The liquid, however, shows only continuous absorption in the region on the longer wavelength side of 3300A (Roy,

1960). It was, therefore, thought worthwhile to find out whether bands are produced in the absroption spectra also of these compounds in the solid state at low temperatures. The results of investigations on the absorption spectra of *m*-chlorotoluene and *p*-chlorotoluene in the solid state at about −130°C have been discussed in the present paper.

EXPERIMENTAL

As the singlet→triplet absorption is very weak, a cell of thickness about 10mm. had to be used in each case. The cell was made of Pyrex glass and the thin windows were made by blowing the ends of a tube. When *m*-chlorotoluene or *p*-chlorotoluene contained in such a cell is frozen by immersing the cell in liquid oxygen an opaque mass is obtained. Attempts were therefore made to obtain at least a semi-transparent frozen mass in each case by cooling the liquid slowly to a temperature just above the melting point of the crystal and then by slowly lowering the temperature a few degrees below the freezing point. No single crystal was produced by this method, but almost a transparent mass with a few internal cracks was obtained. The liquids were of chemically pure quality supplied by B.D.H. of London. The vertical straight portion of a 250-watt coiled tungsten filament lamp was used as the source of light and it was focussed with a lens on one of the windows of the cell. The light transmitted through the other window was focussed on the slit of an Adam Hilger medium quartz spectrograph giving an inverse dispersion of about 10A/mm in the 3500A region. An exposure of about eight hours was required to photograph the absorption spectrum. On each spectrogram iron arc spectrum was also photographed as a comparison.

Microphotometric records of the spectrograms were taken using a Moll self-recording microphotometer. Two sharp scratches made with a razor blade along two chosen iron lines on each of the spectrograms were extended across the absorption spectrum and the wavelengths of the absorption maxima were measured from the microphotometer records of the absorption and iron arc spectra by measuring the distances of the maxima from the positions of the chosen iron lines and finding out the wavelengths of the iron lines at such distances on the record of the iron arc specrum. As the bands were found to be broad, care was taken to locate the positions of the maxima with reasonable accuracy.

RESULTS AND DISCUSSION

Microphotometric records of the absorption spectra are reproduced in Fig. 1. The record of the spectrum of the incident light photographed with suitable exposure is also reproduced in the figure. The wave numbers of the bands are given in Table I.

TABLE I

Metachlorotoluene			Parachlorotoluene		
No.	ν in cm^{-1}	Assignment	No.	ν in cm^{-1}	Assignment
A	24885	0,0	A	26200	0,0
B	25830	0+945	B	26810	0+610
C	26775	0+2×945	C	27230	0+1030
D	27720	0+3×945	D	27750	0+1550
			E	28260	0+2×1030

Metachlorotoluene

The band at 24885 cm^{-1} (4017.4A) is very weak but it is definitely present in the different spectrograms obtained for *m*-chlorotoluene. The frequency of this band is very near to that of the first broad fluorescence band at 24862 cm^{-1} reported by Biswas (1956a). Thus in this case the 0, 0 singlet—triplet transition is allowed weakly both in absorption and in fluorescence. The other three bands in the absorption spectrum at 25830, 26775 and 27720 cm^{-1} form a progression of the excited state vibrational frequency 945 cm^{-1}. Probably the corresponding ground state frequency is 996 cm^{-1}, as can be seen from the fact that the strong Raman line 996 cm^{-1} is assigned to the breathing mode of the ring. Thus this symmetric mode is coupled to the singlet→triplet transition in this molecule which as a whole has neither a centre of symmetry nor a strict two-fold axis.

It would be of interest to find out what vibrational frequencies are associated with the singlet←triplet emission. The frequencies of first three fluorescence bands reported by Biswas (1956*a*) are 24862, 23578 and 23115 cm^{-1}. All these bands are very broad and the third is the strongest. If the centre of the second band would be taken at 23646 cm^{-1} the difference of the first two frequencies would agree with the Raman frequency 1216 cm^{-1} which is due probably to the mode 2 of the ring. The next band would then be assigned as $\nu_0-(1216+531)$. The frequency 531 cm^{-1} would then agree fairly with the Raman frequency 522 cm^{-1} due to mode 6B of the ring (Pitzer and Scott, 1943). A very feeble band at 4107A is visible in the spectrogram reproduced by him (Biswas, 1956a). Thus the modes associated in the emission spectrum are different from those associated in the corresponding singlet→triplet absorption in this case.

Parachlorotoluene

In this case the first band is at 26200 cm^{-1} which is at a distance of 1442 cm^{-1} on the shorter wavelength side from the first fluorescence band at 24758 cm^{-1} (Biswas, 1956b). It appears that in this case the 0, 0 transition in fluorescence does not occur. Probably, the emission is induced by the vibrational mode corresponding to ν_{19B} of the ring. The other bands of the absorption spectrum

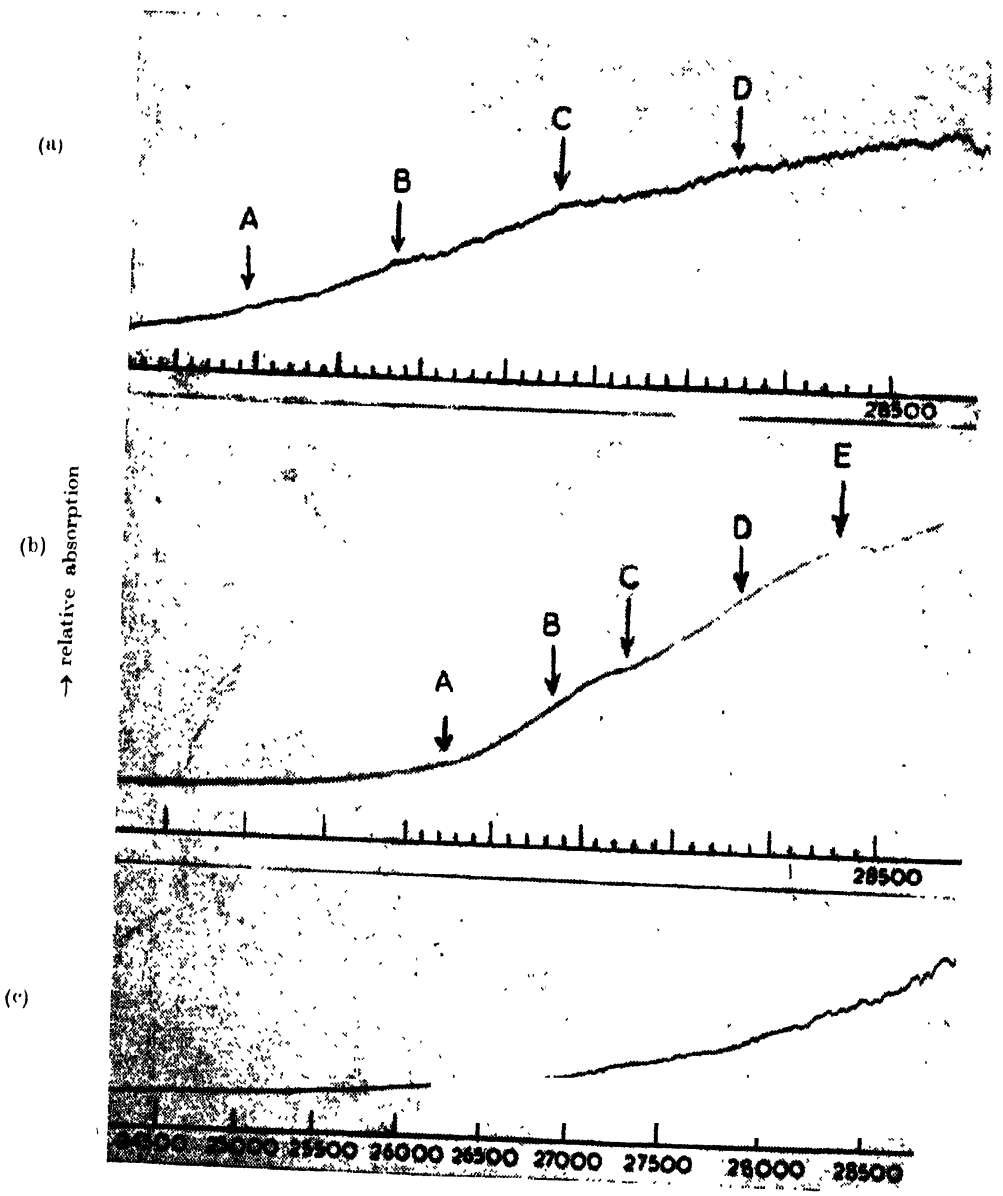

Fig. 1. Microphotometric records of absorption spectra.

(a) Metachlorotoluene at about −130°C.

(b) Para chlorotoluene ,,

(c) Spectrum of incident light.

shown in Table I give the excited state vibration frequencies 610, 1050 and 1550 cm^{-1} respectively. The Raman spectrum of the crystal shows (Sanyal, 1953) strong lines at 630, 1090 and 1590 cm^{-1} and a weak line at 1454 cm^{-1} was also reported by previous workers for the liquid (Magat, 1936). The three lines 630cm^{-1} 1090 cm^{-1} and 1590 cm^{-1} are assigned (Meeke-Kerkhof, 1951) respectively to the modes ν_{6B}, ν_{19A} and ν_{8B} (Pitzer and Scott, 1943). In that case the excited state frequencies 617, 1050 and 1566 cm^{-1} would correspond to the ground state frequencies of modes ν_{6B}, ν_{19A} an ν_{8B} respectively. So, it is found that these modes which make the ring asymmetric to a two fold axis of the ring are coupled to the singlet→triplet transition. In the luminescence spectrum also Biswas (1956b) observed a vibrational frequency 1062 cm^{-1} which might be the frequency 1090 cm^{-1} observed in the Raman effect.

A comparison of these results with those observed in the case of metachlorotoluene leads to the conclusion that asymmetric electronic structure of the ring is the essential requirement for the singlet→triplet transition in absorption and this is produced in the case of metachlorotoluene by the substitution itself and in the case of parachlorotoluene by some asymmetric modes of vibration of the ring.

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